A Rigid Network of Schizophyllan Gel Formed by Addition of Borax

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The aqueous solutions of poly(hydroxyl) compounds with cis-hydroxyl groups like poly(vinyl alcohol) were reported to form gels in the presence of borate. The complexation between borate and two pairs of adjacent hydroxyl groups in two different chains plays the role of crosslinking. Schizophyllan (SPG) is a neutral polysaccharide with a quite rigid triple helical conformation in H2O (persistence length $\approx$ 180nm), which was also found to be gelled by borate in spite of the apparently unfavourable rigid structure for the complexation$^1$. Here we will quantitatively discuss the gelation kinetics and the relationship between gel elasticity and some experimental factors.

![Figure 1](image1.png)  
Figure 1. Gelation process of SPG with borax. $C_{\text{SPG}} = 6\, \text{g/L}$, $C_{\text{borax}} = 32\, \text{mM}$, $[\text{NaCl}] = 1\, \text{M}$, $T = 20^\circ\text{C}$.

![Figure 2](image2.png)  
Figure 2 Dependence of $G'$ and $G''$ on frequency for $C_{\text{SPG}} = 6\, \text{g/L}$, $C_{\text{borax}} = 24\, \text{mM}$, $[\text{NaCl}] = 1\, \text{M}$, $T = 20^\circ\text{C}$.

![Figure 3](image3.png)  
Figure 3 A typical dynamic strain sweep measurement for the SPG-borax gel. $G'$ (□), $G''$ (■), tanδ (○).

Figure 1 shows a representative gelation process for SPG-borax system. The gelation was well fitted by the first order kinetic model with the following form: $G'(t) = G'_{\text{sat}} \left[ 1 - \exp\left( -\left( t - t_0 \right) / \tau_c \right) \right]$, from which gelation time $t_0$, characteristic time $\tau_c$, saturated storage modulus $G'_{\text{sat}}$ can be obtained. It was found that the gelation proceeded faster at higher SPG concentration, higher borax content, higher salt and low temperature. The resultant storage modulus was a linear function of both borax content and SPG concentration. The frequency dependence of storage and loss moduli as shown in Figure 2 was with the hint of the viscoelastic behaviors of Maxwell model in higher frequency range, namely, storage modulus was almost independent of frequency while loss modulus declined with increasing frequency. Figure 3 represents a typical dynamic strain sweep measurement for SPG-borax gel. Before the rupture, a strain hardening stage was observed, during which storage and loss moduli increased with increasing strain whereas tanδ decreased. This kind of elastic behavior should be described by the Langevin-chain network model instead of Gaussian-chain network model. The strain hardening originated from the limited deformability of the rigid SPG chains.

Reference:
A Network of Schizophyllan Constituted by Rigid Wormlike Chains and Dynamic Crosslinks

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Introduction

1. Gelation mechanism of poly(hydroxyl) compounds with borax (e.g. PVA and galactomannans):

\[
\text{Na}_2\text{B}_4\text{O}_7 + 7\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{B(OH)}_3 + 2\text{B(OH)}_4^-
\]

2. Properties of poly(hydroxyl) compound-borax gels.
   
   a. Rehealing ability  \[\text{Nonpermanent crosslinks}\]
   
   c. Liquid-like behavior at low frequencies and gel behavior at higher frequencies  \[\text{Dynamic crosslinks}\]
   
   b. Polyelectrolyte gel \[\text{Introduction of charges during complexation}\]
3. Schizophyllan (SPG) and its gelation mechanism with borax

a. Rigid triple helix in H$_2$O with a persistence length of about 180 nm

b. Gelation mechanism

![Diagram showing gelation mechanism of schizophyllan (SPG) with borax](diagram.png)

Objective of the present work

Poly(hydroxyl) compounds + borax → Rigid Chain (e.g. SPG) → Flexible chain (e.g. PVA) → Gelation behavior??

What’s the difference in Gel properties??
Results and discussion

Fig. 1. A typical gelation process fitted by the first order kinetics

First order kinetic model:

$$G'(t) = G_{sat}' \left[1 - \exp\left(-\frac{(t - t_0)}{\tau_c}\right)\right]$$

$t_0$, gelation time
$\tau_c$, characteristic time
$G_{sat}'$, saturated storage modulus

G’ is almost independent of $\omega$ while G” decreases, with a hint of Maxwell model behavior at high frequencies.

Fig. 2. A typical dynamic mechanical spectra for SPG-borax gel.
The storage modulus is proportional to borax content (crosslinker content).

Gelation proceeds faster with increasing borax content.
Fig. 4. SPG concentration dependence

(a) SPG concentration dependence

G (Pa)

Cp (g/L)

0 400 800 1200
0 500 1000 1500 2000 2500 3000 3500 4000

Cb = 24 mM
Cb = 16 mM

G, \text{sat} (Pa)

Time (min)

0 400 800 1200
0 500 1000 1500 2000 2500 3000 3500 4000

(b) Possibility of crosslinking

\( G \propto (C_p)^n, n = 1 \)

Possibility of chain-chain contacting

Chain flexibility

SPG (n = 1)

Galactomannan (n = 2.6)

PVA (n = 4.7)

large

high

flexible

small

low

rigid

(c) Possibility of chain-chain contacting
The obtained crosslinking enthalpy is larger than that of PVA-borax, indicating the less dynamic nature of crosslinks.

The Arrhenius treatment gives a negative activation energy, attributed to the exothermic nature of complexation equilibrium.

\[ G = 2c_iRT = 2c_i\exp\left(-\frac{\Delta H}{RT}\right)RT \]
Accelerating ability: Li$^+$ < Na$^+$ < K$^+$ < Cs$^+$
Ba$^{2+}$ and Ca$^{2+}$ tend to precipitate borate ions, therefore no gelation!
The poor rehealing ability reflects the less dynamic crosslinks present in SPG-borax gel. The strain-hardening could originate from the poor extensibility of rigid triple-helical SPG chains.
## Conclusion

### The Differences between Gels Made of Rigid and Flexible Chains

<table>
<thead>
<tr>
<th></th>
<th>Induction time</th>
<th>Crosslinking enthalpy</th>
<th>Rehealing ability</th>
<th>Dynamic spectra</th>
<th>Polymer conc. dependence of elasticity</th>
<th>Strain hardening</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPG-borax gel (rigid)</td>
<td>Yes</td>
<td>Large</td>
<td>Poor</td>
<td>Rubber-like</td>
<td>Low</td>
<td>Yes</td>
</tr>
<tr>
<td>PVA-borax gel (flexible)</td>
<td>No</td>
<td>Small</td>
<td>Good</td>
<td>Liquid-like at low $\omega$</td>
<td>High</td>
<td>No</td>
</tr>
</tbody>
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